

(12) UK Patent Application (19) GB (11) 2 339 785 (13) A

(43) Date of A Publication 09.02.2000

(21) Application No 9813786.2

(22) Date of Filing 26.06.1998

(71) Applicant(s)
KNI Limited
(Incorporated in the United Kingdom)
Albany Road, GATESHEAD, NE8 3AT, United Kingdom

(72) Inventor(s)
Michael Ellis

(74) Agent and/or Address for Service
KNI Limited
Albany Road, GATESHEAD, NE8 3AT, United Kingdom

(51) INT CL⁷
C09D 5/33 127/06

(52) UK CL (Edition R)
C3V VABR VACH VACR VDQ VEB

(56) Documents Cited
EP 0486319 A1 EP 0305074 A2 WO 99/04098 A1
BE 000892056 A
WPI Abstract Accession No. 1989-361148 &
JP120071436A

(58) Field of Search
UK CL (Edition Q) C3V VABN VABQ VABR VACH
VACN VACQ VACR VDQ VEB
INT CL⁶ C08K 3/40 , C09D 5/33 127/06
ONLINE: WPI, JAPIO, EPODOC

(54) Abstract Title
Retroreflective PVC coatings

(57) This invention relates to methods of producing retroreflective coatings, materials, and products using vinyl dispersions. The retroreflective compositions comprising of dispersions of polyvinyl chloride resins, plasticizers, stabilizers, colour pigments, adhesion promoting agents, refractive and retroreflective constituents, fillers and additives, which when applied to a substrate and subjected to heat, are converted from liquid dispersions to thermoplastic solids offering retroreflective properties. The retroreflective elements are preferably glass or acrylic and are at least partially coated with reflective material.

GB 2 339 785 A

The claims were filed later than the filing date but within the period prescribed by Rule 25(1) of the Patents Rules 1995.

The print reflects an assignment of the application under the provisions of Section 30 of the Patents Act 1977.

**THE PRODUCTION AND APPLICATION OF
RETROREFLECTIVE VINYL DISPERSION
COATINGS AND MATERIALS**

FIELD OF INVENTION

This invention relates to methods of producing retroreflective coatings, materials, and products using vinyl dispersions, and application methods of retroreflective vinyl dispersions to substrate materials.

BACKGROUND OF THE INVENTION

Retroreflective coatings and materials are well known and have been in use for many years as a means of increasing night time visibility of pedestrians and roadusers and as a means of enabling static objects, such as traffic control and hazard warning devices, to be clearly visible to oncoming vehicle drivers during the hours of darkness.

It is known to manufacture a reflective material by coating a carrier sheet with a releasable adhesive and applying a continuous layer of transparent microspheres to the adhesive. The exposed surfaces of the microspheres are then coated with a reflective metallic layer, such as aluminium, a sheet coated with a permanent adhesive is then applied over the metallic surface, the two sheeting layers are then separated, the microspheres being retained in the permanent adhesive coated layer to produce retroreflective sheeting, as an alternative the metallic layer is omitted and metallic flake or pigment is included in the permanent adhesive to provide reflectivity. Another method is to coat a carrier web with a permanent adhesive which incorporates metallic flake or pigment and then transparent microspheres are applied over the whole surface area. The reflective sheeting materials are then cut into strips or shapes for attaching to garments or other products. Reflective sheeting materials, while offering satisfactory

results, are limited in use, particularly in the construction of garments as the materials are unsuitable for large areas, limited in colours and are not aesthetically pleasing, and when used as traffic control products the materials are rigid and generally attached to a smooth clean surface, furthermore, shapes and designs must be cut from a larger section which results in considerable material wastage.

A more recent method of producing reflective materials is to include glass microspheres partially coated with aluminium, in aqueous based pastes, which are then applied to fabrics by screen printing. However, aqueous based systems have a number of problems, firstly they are principally limited to use on absorbent textiles, some of the chemicals that must be used in aqueous formulations are not compatible with aluminium and tend to have adverse effects on the reflectivity and usable life of the product, furthermore, the chemicals used to create cross-linking cause the paste to gel during storage which limits the pot life to a short period. Aqueous systems are intended for the continuous screen printing of textiles and when used for individual item printing have an extremely limited life of only a few minutes before drying in the screen if printing is interrupted, as a result the screens must be thoroughly cleaned at every stoppage, increasing time and production costs. Aqueous systems also require lengthy and accurate time and temperature control during drying and curing, which results in a slow production rate and limits their use to relatively few printers with the necessary equipment.

It is therefore an object of this invention to provide a method of producing retroreflective coatings and materials, that effectively overcome the existing problems associated with reflective sheeting materials, and with aqueous and solvent based liquid reflective systems. The invention provides a method of producing retroreflective vinyl

dispersions which do not appreciably detract from the normal daytime appearance or handle of the substrate or product, and that can be applied by conventional methods without the need for special equipment or facilities, that can be applied to numerous materials and substrates, and incorporated into the manufacture of vinyl based products. And unlike with aqueous and solvent based systems, the curing or fusion of the liquid retroreflective vinyl dispersions is a physical action rather than a chemical reaction, and as a result the formulations will have a long term usage life when stored and will remain in liquid form when in printing screens and coating equipment. Furthermore, formed retroreflective materials and articles can be produced either individually or by continuous production methods, and substrates can be printed or coated either continuously or individually without the need for equipment cleaning during stoppages of any length of time. The formulations can be coloured and applied to a substrate sequentially in predetermined areas to produce single or multicoloured designs and patterns, without the necessary wastage that occurs when using sheeting materials. The liquid dispersions may be applied to a substrate, either temporarily or permanently, partially fused and then fully fused at a later stage, such as when producing transfer prints and coatings. Also, the chemicals used in the formulations do not adversely affect the reflective constituents, or reduce the retroreflective performance of the finished products.

DESCRIPTION OF THE INVENTION

Retroreflective vinyl dispersions may be used in various processes, including screen printing, spread coating, moulding, heat transfer, continuous rotary and flat-bed printing, individual item printing, knife, roll, curtain and saturation coatings, strand and

spray coating, extrusion, dipping, casting, slushing, cavity in place moulding, and other coating and production processes. These techniques take advantage of the convertibility of the dispersions from a liquid to a thermoplastic solid, and the ability to formulate without volatiles.

Vinyl dispersions that contain little or no volatile thinners or diluents are known as plastisols. In some formulations the liquid phase of the dispersion is extended with volatile dispersants or thinners which are removed during the fusion process, these are known as organosols. For the purposes of this process, the term vinyl dispersions, is intended to include both plastisols and organosols.

The retroreflective properties of the vinyl dispersions are achieved by including various ingredients in the formulations, which when used separately or combined, result in retroreflection. Principally, transparent microspheres are used. The microspheres should have a high degree of roundness, the more perfect the sphere, the better the retroreflection, irregular shaped or marked spheres may result in diffused reflection. The microspheres may be manufactured from transparent clear or coloured materials, preferably glass, though other materials such as acrylic, or the like, may be used.

The microspheres should have a refractive index of between a 1.3 and 2.5, generally, three types of microspheres are commercially available, 1.5, 1.9, and 2.2, the particular refractive index used, or combination of differing refractive indices used, will depend on the refractive index and thickness of the cured/fused dispersions and any additional layers that may be applied to the final product. For most purposes concerning this process, microspheres with a refractive index of around 1.9 are used.

The size of the microspheres used in the dispersions depends on the method of application and the use of the final product. The microspheres will preferably have a

size range of between 5 and 250 microns in diameter, for most purposes concerning this process, the microspheres will have an average diameter of 50 microns or less.

The quantity of microspheres used in the dispersions, is determined by the type of microspheres used, the method of application, the use of the final product, and the level of retroreflection required. The microsphere content of a dispersion may be between 5 to 300 phr (parts per 100 vinyl resin), though generally will average 50 phr or less.

Microspheres which are partially coated over one hemisphere with reflective materials provide the optimum reflectivity. Light is refracted as it enters a sphere, the light is then reflected or refracted at the rear coated surface of the sphere, and is then refracted again as it leaves the sphere, resulting in retroreflection. The angles of refraction and reflection are determined by the characteristics of the sphere.

The partial coatings for the microspheres may be aluminium, silver, alloys, oxides, or other metallic or chemical compounds. The microsphere coatings may be applied by vapour or chemical deposition, though other methods may be used.

Another method is to partially coat the microspheres with multiple layers of alternating high and low refractive index materials, such as layers of zinc sulfide and magnesium fluoride, or similar materials. The partial coatings of the microspheres may be applied by vapour or chemical deposition, though other methods may be used.

A further method is to partially coat the microspheres with a transparent coating containing reflective particles, such as metallic flake, metal oxides, nacreous pigment, titanium dioxide, or other refractive or reflective materials.

To achieve a satisfactory degree of retroreflection using uncoated microspheres, it is necessary to include larger quantities of microspheres within the dispersions,

generally between 100 to 200 phr. A combination of partially coated and non-coated microspheres may be used.

Reflection may be increased by applying a pigmented underlayer of a light colour, or using a base which includes particles such as metallic flake, metal oxides, nacreous pigment, titanium dioxide, or other refractive or reflective materials, prior to the application of the dispersion containing the microspheres.

Reflection may also be increased by including materials such as metallic flake, metal oxides, nacreous pigments, titanium dioxide, or other refractive or reflective materials, combined with microspheres, within the dispersion.

The inclusion of materials such as coated and non-coated microspheres, metallic flake, metal oxides, nacreous pigment, titanium dioxide, or other refractive or reflective materials, may also be used to provide decorative and special visual effects if incorporated into one or more of the layers when single or multiple coatings are applied to a substrate, and may include ingredients that are only visible when viewed in particular lighting conditions, such as infrared, ultraviolet, or the like.

Vinyl dispersions are fluid suspensions of fine-particle-size polyvinyl chloride resins in liquid/diluent systems. The viscosity of the vinyl dispersions may range from a pourable liquid to a paste. The polyvinyl chloride polymer resin is usually in a white powder form and the plasticizer is a clear oil like liquid which provides flexibility. When mixed and subjected to heat at around 150°-170°C (302° - 338°F), the dispersion turns into a homogeneous hot melt, the resin begins to absorb the plasticizer until it reaches a saturation point when the two ingredients fuse to form an elastomer film. When the hot melt is cooled to around room temperature (25°C / 77°F), it becomes a tough vinyl product. However, in this form the film is particularly unstable, and therefore additives

are included to prevent the film from cracking and discolouring when heated, to modify the viscosity, increase the durability, and to retain the retroreflective constituents.

The ingredients for the vinyl dispersion formulations for this process vary with the method of application of a coating and the particular substrate, the article or the product being formed and the manufacturing methods. The formulations generally include polyvinyl chloride resins, plasticizers, stabilizers, fillers, pigments, adhesion promoting agents, refractive and retroreflective ingredients.

Each of the ingredients, separately or collectively, in the formulations, can affect the retroreflectivity of the final fused coating or product, and careful selection is necessary to achieve satisfactory results.

It is important that the correct resin is selected. The resin must offer maximum clarity and transparency, and when fused must be flexible and durable. Resins for the vinyl dispersions are different from general purpose suspension resins designed for calendaring, extrusion or injection moulding, these resins tend to have a large particle size, are very porous and coarse, and will not readily form pastes below 100 phr (parts per hundred vinyl resin) plasticizer. The vinyl dispersion resins are polyvinyl chloride homopolymers and copolymers produced via emulsion or micro-suspension polymerization processes. During polymerization, the distribution of particles formed is in the range of 0.2 to 15 microns, secondary particles (grains) in the range of 5 - 60 microns are formed during stripping, dewatering and drying, and grinding operations. The particle size distribution can be monomodal, bimodal, or multimodal. The particle size has a significant effect on the formulation rheology. If the particle size distribution is very narrow the paste viscosities at both low and high shear will be dilatant, as the particle size distribution is broadened, the paste flow will be more shear-thinning

(pseudoplastic) and in general lower than the paste viscosity at a higher shear. Therefore, it may be necessary to blend more than one resin to control paste viscosities.

Special suspension resins, known as extender or blending resins, are significantly finer in particle size than general purpose suspension resins. Extender resins are less porous, form melts without mastication, and when combined with dispersion resins, control paste viscosity, gloss, gelation and other plastisol properties, and in highly plasticized formulations, extender resins provide a drier feel to the finished product. The use of copolymer blending resins will help to accelerate gelation and fusion, however, for this process, blending resins have a detrimental effect on the transparency of the fused films, increasing opacity which results in reduced retroreflectivity. Copolymers are available with 5% to 10% vinyl ester content, increasing the vinyl ester content has the effect of lowering the fusion point, but results in reduced film strength. Blending resins must be used sparingly.

Dispersion resins range in viscosity (I.V.) from 0.7 to 1.45. As the molecular weight increases, many properties are affected. Increasing the molecular weight leads to increased fusion strength, but slower gelation. It increases the viscosity of a vinyl melt, resulting in reduced flowout on coatings and mouldings. Although changes in molecular weight affect the fused product strength, they have little influence on the fusion temperature, the fusion temperature is affected by the inclusion of comonomers such as vinyl acetate, which break up the crystalline structure in the polymer.

Residual emulsifiers and/or surfactants remaining on the dispersion resins will have a detrimental effect on the properties of the paste, such as reduced clarity and reflectivity, also higher viscosity and poor compatibility with thermal stabilizers.

It has been found that functionally active resins, such as those with properties

attributable to carboxyl groups on the vinyl chain, provide optimum durability and performance of the fused film when partially metallized microspheres are included in the formulations. The carboxyl functionality increases adhesion to a number of materials, including fabrics, plastics, metals and alloy substrates.

Adhesion to various substrates may be increased with the inclusion of small amounts (10 to 20 phr) of solution resin, substituted for dispersion resins. Solution resins are vinyl copolymer resins produced by a solvent process, these resins may have carboxyl, hydroxyl or other functionalities, that when crosslinked with epoxy, melamine, or other adhesion promoters, provide increased adhesion.

The selection of a plasticizer, or blend of plasticizers, is crucial to the overall performance of the reflective vinyl dispersions, plasticizers provide flexibility and affect the finished properties, for the purposes of this process, optimum clarity is also an essential feature. Plasticizers enable the molecular chains of polymers to move freely with respect to one another, acting as an internal lubricant and overcoming the attractive forces between the chains and separating them to prevent intermeshing. The higher the temperature, the greater the penetration of plasticizer between the chains and the greater the melt flow or mouldability.

Plasticizers used in the retroreflective vinyl dispersions should be esters. They may be esters of long chain alcohols with aromatics such as phthalic anhydride, with straight-chain dibasic acids such as sebacic, azeleic, or adipic, or with phosphoric acids; or they may be polyesters such as those based on propylene glycol and sebacic acid. Higher aromaticity means a higher relative ability of the plasticizer to interact with the resins.

Phthalate ester, such as di-2-ethylhexyl phthalate (DOP) has been found to be

particularly suitable. Shorter-chain-alcohol phthalate esters, such as dihexyl and dibutyl phthalates, are more volatile but fuse faster in the dispersions due to their higher percent of aromaticity. Longer-chain-alcohol phthalates may also be used, primarily for their low volatility. Linear-alcohol phthalates, based on 7 to 11 carbon alcohols, provide lower dispersion viscosities and slightly better low temperature properties than DOP.

Phosphate esters, such as tricresyl phosphate (TCP) and octyldiphenyl phosphate, are highly solvating and may also be used. These esters, with the exception of trioctyl phosphate (TOF), offer higher initial and aged viscosities and lower fusion temperatures when compared with DOP. Phosphates also offer some degree of flame resistance through increased char formation during combustion.

Other highly solvating plasticizers that offer good strength properties with low fusion temperatures are butyl benzyl phthalate, dihexyl phthalate, diisohexyl phthalate, and esters of benzoic acid. These plasticizers are used with copolymer dispersion and extending resins to achieve usable physical properties at fusion temperatures below 138°C (280°F).

Specialized monomeric esters such as trimellitates, including trioctyl trimellitate (TOTM), trisooctyl trimellitate (TIOTM), triisononyl trimellitate, and similar esters of linear alcohols, offer low volatility and resistance to extraction by solvents and oils, as do polymeric plasticizers, such as polyester of propylene glycol and sebacic acid. These plasticizers are generally very viscous and are usually blended with lower viscosity plasticizers.

Epoxy, polymeric and citrate plasticizers all lend themselves to either primary or secondary use, other materials can also be used as vinyl dispersion plasticizers, such as liquid nitrile rubber which offer oil resistance and can be vulcanized. Low volatility

acrylate monomers such as triethylene glycol dimethacrylate offer flexibility to the liquid dispersions and during fusion cure to a hard polymer. Epoxidized soya and linseed oils offer heat and light stabilization properties as well as plasticization properties, but should be used in small quantities as their inclusion can result in loss of transparency and can effect the retroreflective properties of the formulation.

Polyvinyl chloride is an extremely heat sensitive polymer. If the polymer is processed without stabilizers it will begin to degrade, initially yellowing followed by further discolouration, evolution of hydrochloric acid and crosslinking, and eventually complete degradation. The correct selection of the stabilizer or blend of stabilizers is critically important, more than any other ingredient in the formulations the stabilizers may affect the transparency of a fused formulation and restrict retroreflectivity.

A primary stabilizer is described as one that, when used as the sole stabilizer, offers an acceptable degree of heat stability. The primary stabilizers are leads, mixed metals, and organotin stabilizers. A secondary stabilizer is one that cannot be used as the sole stabilizer, but can extend, compliment or improve the stability of the polyvinyl chloride when used with the primary stabilizer. Secondary stabilizers are generally epoxidized oils and metallic soaps.

The preferred stabilizers for the retroreflective vinyl dispersions are barium based. Although cadmium, and zinc salts of long-chain fatty acids such as stearic, oleic, benzoic, and lauric acids are also suitable, individually or as blends.

Lead based materials such as dibasic lead phosphite, tribasic lead sulfate, and lead stearate are excellent stabilizers, but their use is limited for this process as they result in increased opacity and therefore affect the level of retroreflectivity.

Most stabilizers used for reflective vinyl dispersions are in liquid form, if solid

stabilizers are used they must be predispersed in plasticizer prior to their inclusion.

Antioxidants and ultraviolet stabilizers may be added to minimize degradation during long term exposure to ultraviolet light and weathering.

The rheology of the vinyl dispersions is an important feature. The liquid needs to flow around the retroreflective microspheres when applied to the substrate, to allow the microspheres to settle-out and for the film to form an even coating over the surface of the substrate, particularly when applied to materials produced from fibres or filaments, to ensure that the dispersion penetrates the interstices of the material. Two types of volatile organic materials may be used to control the rheology of the retroreflective vinyl dispersions, diluents and dispersants. Diluents are poor or non-solvents and may be aliphatic, aromatic, or a mixture of both. They do not contribute to the resin solvation and in most cases must be evaporated at temperatures below the complete fusion of the dispersion to prevent blisters, bubbles or cracking. Mineral spirits are aliphatic diluents and have been found to be particularly effective. Xylene and toluene are aromatic diluents, a number of commercially available diluents may also be used.

Dispersants are stronger volatile solvents. Unlike diluents, dispersants help to solvate the resin particles and are helpful in developing fusion properties. Because of their high solvency, dispersants tend to increase viscosity rapidly and as such are never used alone, typical dispersants are diisobutyl ketone, methyl isobutyl ketone, methyl ethyl ketone, isophorone, cyclohexanone, diacetone alcohol and butyl carbitol, though others may be used.

The vinyl dispersions should be formulated to contain a balance of diluents or diluents-dispersants, blended to obtain rheology control and good fusion properties. Generally between 0 to 5 phr should be added, greater amounts can affect the metallic

coatings on the microspheres which will result in a loss of reflectivity.

Polymers, plasticizers, stabilizers, solvents and diluents are considered the main vinyl dispersion components. If the dispersion properties are to be modified, these ingredients should be the first to be altered, however, changing any one of these ingredients may have adverse effects on the other properties, particularly retroreflectivity. There are a number of chemical materials that may be used in modifying the viscosity and the processing the vinyl dispersions when used in low concentrations (1 to 2 phr), without significantly sacrificing other properties. Viscosity reduction using modifiers does have disadvantages, such as loss in film clarity and a detrimental effect on heat stability, generally, low levels (>2 phr) will have minimal side effects.

Viscosity depressants are liquid surface active agents that act by reducing the interparticle structure in the dispersion. They are extremely effective when the dispersion is highly filled, such as reflective microspheres, by aiding the wetting of the surfaces of the microspheres. Most viscosity depressants are non-ionic or anionic type surface active agents, chemical compounds such as ethoxylated alcohols, fatty acid esters, aliphatic compounds, and lecithin-based derivatives, have been found helpful in reducing the viscosity of reflective dispersions.

There are some applications where high viscosity and a high degree of thixotropic properties are required. Low levels (<5 phr) of thickening agents may be incorporated into the dispersions, organo-metallic complexes (Ircogels) are particularly effective as they provide sag-resistant dispersions with a high degree of thixotropy and are particularly suited to retroreflective formulations because of their high degree of clarity. Fumed and precipitated silicas, bentonite clay, special clays, ultrafine calcium carbonites, and others, may also be used as thickeners, though the amounts should be

kept to a minimum to avoid loss of reflectivity.

Liquid nitrile rubbers may be used in specific dispersions to reduce plasticizer migration and improve low temperature impact, cut through resistance, and increase abrasion resistance, though again the amounts used should be kept to a minimum as retroreflectivity can be affected.

Due to the unusual nature of the retroreflective vinyl dispersions, it may be necessary to include a number of additional ingredients in the various formulations. The particular ingredients used, will depend on the individual formulation, the method of application or production, and the end use of the finished product.

A common feature with all the dispersions is the use of microspheres, these are relatively large particles, to ensure that they remain secured to the substrate within the fused dispersion and resist abrasion, it is generally necessary to include adhesion promoting agents in the formulations. Silanes have proved to be particularly effective, as an alternative, epoxy resins, modified phenolic and hydrocarbon resins, titanates, alkyl phosphate ester, zirconates and stabilized metal based adhesion promoters, or similar, may be used.

It may also be necessary to include lubricants to optimize the stabilizer system, allowing processing at reduced temperatures and increasing crosslinking, these may be in the form of internal or external lubricants or bifunctional. Surfactants may also be included in the formulations as processing aids to achieve particular results.

Abrasion resistance can be increased by secondary coating the retroreflective dispersions with surface layers such as polyurethane, fluorocarbon, paste, or the like. The secondary surface layer may include various ingredients to achieve particular effects, such as colour pigments, microspheres, mica platelets, metallic or oxide flakes,

particles, and others, either separately or as combinations.

During the preparation of the dispersions, the intention is to break up the loose agglomerates present in the solid ingredients and to disperse them homogeneously through the liquid medium. To achieve good dispersion, the solids must be subjected to shearing action in contact with the liquid medium. It is important that the temperature of the dispersion during the mixing is maintained below 32.2°C (90°F) otherwise it can result in too rapid solvation of the resin particles, poor viscosity control, and premature fusion of the resin particles. The vinyl dispersion will generally contain air unless the mixing is performed in a vacuum chamber, if a vacuum cannot be pulled in the mixing chamber, a vacuum should be applied to the dispersion in a separate vessel. The vinyl dispersions should be filtered through 60 to 100 mesh screens or filter bags, prior to the inclusion of the microspheres and additives, to remove unwetted solid ingredients, dried-up solid particles, fragments and other undesirable contaminants.

The process in which the liquid dispersion is converted into a homogeneous solid upon the application of heat is known as fusion. This conversion is a true fusion of the crystallite structures in the polymer particles, followed by solution of the molten polymer in the plasticizing vehicle. The mechanical properties (degree of fusion) development of the vinyl compound is a time-temperature phenomenon. The fusion temperature of plasticized vinyl is a complex function of the molecular weight, and amount of comonomer, plasticizer level, and polymer-plasticizer interaction parameter. Because the dispersions are fused with heat alone, without mechanical working, the particle size, particle size distribution, and interference from non-vinyl constituents at the particle surfaces also affect the fusion temperature, this is particularly the case with dispersions that include retroreflective ingredients as they also reflect heat during the fusion phase.

Therefore, it is generally necessary to increase the time and temperature by around 10% over the normal, this allows the materials to reach the required temperature and to compensate for the loss of reflected heat. The retroreflective vinyl dispersions may be fused by various devices, including ovens and heated chambers, heat platens, heat rolls, radiant resistance rods or quartz lamp heating. The crystallites in the polyvinyl chloride, melt over a fairly wide temperature range, so some strength is developed at temperatures below the ultimate fusion point, this strength cannot be increased by increasing the time of heating. If the fusion does not take place completely, the results can be loss of performance and durability, and increased opacity with a resulting loss of reflectivity.

Vinyl dispersions for printing and coating applications have to be formulated to behave as a solid and should not drip when applied, the dispersions should flow easily and should level well after deposition, but in order to give a sharp image must not exhibit excessive flow. Importantly, the reflective and refractive ingredients must be retained within the final fused product, and withstand abrasive treatment without significant loss.

The retroreflective vinyl dispersions, by necessity must have excellent clarity. As a result of this transparency, even though the dispersions can be colour pigmented the underlying colours of the substrate may be visible and affect the appearance of the final product, therefore the dispersions are ideally suited to lighter coloured substrates, when applied to dark coloured substrates it may be necessary to apply an opaque light coloured base prior to the application of the retroreflective dispersions. The underbase may be applied over the total area of the substrate or applied as sections or patterns to achieve particular effects, half-tone designs have been shown to offer effective results, and the underbase can be of one or more colours to achieve special effects. The

underbase should be gelled, preferably fully fused, prior to the application of the vinyl dispersions to prevent migration of pigments, particles or chemicals between the layers, which may result in reduced retroreflectivity.

Vinyl dispersions are inherently adhesive to many materials, such as cotton and rayon, however, synthetic materials such as nylon and polyester, may require the use of adhesive primers prior to the application of the vinyl dispersions. Nitrile latexes modified with borated casein and nitrile/phenolic solvent systems have been found to be particularly effective primers. Carboxyl resin primer systems increase the adhesion of subsequent top coatings by as much as three or four times that obtained with vinyl chloride/vinyl acetate primers. The primers may also be pigmented and used as underbases on synthetic materials and difficult to coat substrates.

When the retroreflective vinyl dispersions are applied to synthetic fibres, smooth filaments and non-absorbent materials, it may be necessary to include bonding agents in the dispersions. Generally, These are added to a dispersion immediately prior to application and included in amounts of 3 to 8 phr, a number of commercially available products are suitable, in particular iso-cyanurate trimer in di-butyl phthalate bonding agents are particularly effective when the fusion temperatures are above 180°C (356°F).

When printing or coating plastic substrates, such as polypropylene and polyethylene, because their inert non-polar surfaces do not permit any chemical or mechanical bonding to take place, it may be necessary to pre-treat the products prior to the application of the dispersions. Particularly suitable is electrical treatment, where the product is passed between two electrodes and rendered polar and the surface is slightly roughened. An alternative is to pre-treat the products with solvents such as toluene, chlorinated hydrocarbons, or the like. Chemical oxidising agents such as chromic acid,

or similar, may also be used. A further alternative is flame treatment, by exposing the product to an oxidising flame for a short time prior to printing or coating.

Colour pigments may be included in the retroreflective vinyl dispersions, the term pigments also refers to dyes and other particles that result in producing colours. It is important that the pigments used do not adversely affect the stability of the dispersions and do not degrade in the environment that the product will be subjected to. Importantly for reflective dispersions, it is critical that the pigments used do not reduce the transparency of the final fused coatings. The pigments may be organic or inorganic in nature and should be milled to a very fine particle size, the pigments should preferably be materials that are soluble in polyvinyl chloride polymer and enter into the polymer matrix during the fusion process. Speciality pigments such as metallics, pearlescents, fluorescents, phosphorescents, and other materials, may also be included in the dispersions, though these may result in a reduction in retroreflectivity. The quantity of colour pigment in the dispersion will affect the colour of the reflected light, generally, lower quantities of colour pigment will result in an appearance of white reflected light, as the quantities of colour pigment are increased in a dispersion the colour of reflected light becomes that of the colour pigment, the greater the quantity of pigment, the deeper the colour of the reflected light.

A further method of achieving special visual effects, is to apply two or more layers of dispersions, the layers being applied sequentially and either partially or wholly covering the underlying layers. The layers may be vinyl dispersions or a combination of vinyl dispersions and other paste systems. Each layer may be of the same or a different refractive index, and may be of differing levels of transparency, and may be clear, or include colour pigments, coated or uncoated microspheres, mica platelets, metallic or

oxide flakes, particles, and others, and may include ingredients that may only be viewed under particular lighting conditions, such as infrared, ultraviolet, and the like, either separately or combinations.

Vinyl dispersions are particularly suitable for application to substrates by screen printing. Screen printing is widely used for the coating and decoration of fabrics and plastics, good quality multicolour printing is possible, including the coverage of large surface areas, the coatings are relatively heavy, therefore good coverage and abrasion resistance are obtained.

For individual item printing, generally the screen consists of a stencil bonded to a fine weave material and tensioned in a frame. The vinyl dispersion is pushed through the screen openings by a squeegee and deposited on to the substrate surface. The squeegee is a shaped flexible blade in a holder. The substrate is then passed through a heated chamber or through a heating device to fuse the printed dispersion, ensuring that adequate time is allowed for the dispersion to reach the fusion temperature of around 160°C (320°F). The screen printing equipment may be manually operated units or completely automated machines. It has been found that retroreflective dispersions are preferably applied using a screen mesh with openings two to three times the size of the largest particles, generally the microspheres, to avoid blockages, and the dispersions are best applied using single pass, off-contact strokes with a single flood stroke between prints, multiple strokes may reduce reflectivity. Multicoloured prints should be fully fused between colours, inadequate fusion may result in loss of reflectivity in overlapping areas and cause screen blocking. Wet-on-wet printing may be carried out for low quantity runs, the screen must be cleaned periodically to prevent build-up and blocking.

Retroreflective vinyl dispersions may also be applied using continuous screen

printing methods, either rotary or flat-bed equipment may be used, although the printing principals are similar to individual item printing, the substrate is generally in roll form and travels past the screens using an unwind-rewind operation.

The retroreflective dispersions may be applied over the whole surface area of the substrate, or in selected designs and patterns, and may be single or multiple colours. Discontinuous coatings provide maximum abrasion protection for minimum coating weight, and offer breathability and moisture permeability. The preferred viscosity of the screen printing dispersions is between 12000 to 25000 centipoise, depending on the printing methods and equipment.

Screen printing may also be used to produce retroreflective transfer coatings and designs, transfer prints may be applied using individual or continuous printing methods, using manual or automatic, rotary or flat-bed equipment. The dispersion formulations and printing methods are similar to conventional screen printing, except that the substrate is generally a release or casting paper, though other materials may be used, coated with a thermo-set resin, silicone, or other material, and the designs and images are printed onto the release paper in reverse order, starting with the eventual outer surface layer. Each layer is gelled before the application of the next, and importantly, the dispersions are only partially fused at temperatures of around 93°C (220°F) during printing. The printed release or casting material, is then applied to the substrate, with the print adjacent to the surface of the substrate, and is then subjected to heat at around 150°-170°C (302°- 338°F) and pressure to reactivate and fully fuse the vinyl dispersion to the substrate. The release paper is then peeled away to reveal the correctly facing printed image on the substrate. The release or casting material may be embossed or patterned to create different effects on the outer surface. Both hot and cold peel methods

may be used, though hot peel offers improved reflectivity as part of the image remains on the release or casting material, exposing a greater number of retroreflective microspheres. The inclusion of small amounts of commercially available puff additives may increase the retroreflectivity by roughening the surface of the fused dispersion.

For transfer printing on to dark coloured substrates, a light coloured opaque print may be applied as the final print on the release or casting material to provide a base for the transparent retroreflective dispersions when the transfer is reversed on the substrate. The base may include particles such as metallic flake, metal oxides, nacreous pigment, titanium dioxide, or other refractive or reflective materials.

The dispersions may be applied to the release or casting materials in single or multiple layers, either as sections or as all over coverage. The inclusion of materials such as coated and non-coated microspheres, metallic flake, metal oxides, nacreous pigment, titanium dioxide, or other refractive or reflective materials, may also be used to provide decorative and special visual effects if incorporated into one or more of the layers, and may include ingredients that are only visible when viewed in particular lighting conditions, such as infrared, ultraviolet, or the like.

Fabric, paper, metal, and other substrates may be coated with retroreflective dispersions by a process that in its simplest form, consists of let-off and take-up equipment, a coating head, a fusion zone, and optional embosser, and a cooling zone. The most common types of knife coating are knife-over-roll, floating-knife, and knife-over-blanket, all depend on the clearance between the coating blade and the web for the coating thickness, because there is a fixed gap between the blade and the web, continuous, accurate coating thicknesses can be obtained. The knife angle has little effect on thickness, but the angle may be varied to change the quality of the coating, by

using one or more knife coating methods in combination, and controlling the knife configuration, knife angle, and web tension, it is possible to apply uniform retroreflective coatings to non-uniform substrates and produce a variety of surface patterns. The first coater applies a heavy non-reflective fill-coat and levels out the substrate, the second coater applies a thin retroreflective dispersion. Either or both the coats may include colour pigments, and may include materials such as coated and non-coated microspheres, metallic flake, metal oxides, nacreous pigment, titanium dioxide, or other refractive or reflective materials, and may provide decorative and special visual effects if incorporated into one or more of the layers, and may include ingredients that are only visible when viewed in particular lighting conditions, such as infrared, ultraviolet, or the like. In formulating for knife coating, it is necessary to consider both the high and low rheology of the compound. Compounds with a high yield value may be needed to prevent striking into the interstices of the substrate material before and immediately after the web has passed under the knife. True yield can prevent the flow of dispersion from the puddle behind the knife into the interstices of the web, this can be accomplished by transverse backing dams set behind the knife to retain the coating bank in a small area and minimize the bank-to-web contact time.

Retroreflective dispersions may also be applied by roll coating. The simplest roll coating devices are direct or forward roll coaters, the dispersion is picked up or supplied to a roller that travels in the same direction as the web. Roll coating of the reflective dispersions is better carried out by a reverse roll coater in which the complete deposit of coating is wiped off on a web running in the opposite direction to the roll. The applied coating must be fused, temperatures of around 148°C to 177°C (300°F to 350°F) are required. Time at temperature is not a consideration, as fusion is a physical rather than

a chemical phenomenon, however, time to reach temperature throughout the film thickness is critical. The retroreflective vinyl dispersions may be fused by various devices, including ovens, heat platens, heat rolls, radiant resistance rods or quartz lamp heating.

Coating lines can provide for one or more finishing operations on the retroreflective dispersion coated web. Embossing may be carried out in-line, with an engraved steel roll applying pressure to the web as it passes over a rubber backup roll immediately at the oven exit. The fused reflective dispersion must be chilled to set the emboss and allow it to release cleanly from the embossing roll. Alternatively, a coated unembossed material may be reheated by passing it over heated platens and embossed in a separate operation.

Spanishing, the application of a contrasting colour in the emboss depression by means of a tight knife pass and top coating. Top coating protects exposed surfaces from abrasion, dirt, and stain pickup. The top coatings need to be formulated with high molecular weight homopolymers to minimise plasticizer migration from the substrate. Acrylic solution polymers and cellulose acetate butyrate blended with vinyl add to the blocking resistance and dryness of the coating. For other finishing operations, such as printing and flocking, copolymer or carboxy functional dispersions are used as the adhesive. The inclusion of materials such as coated and non-coated microspheres, metallic flake, metal oxides, nacreous pigment, titanium dioxide, or other refractive or reflective materials, to provide decorative and special visual effects if incorporated into one or more of the coatings, and may include ingredients that are only visible when viewed in particular lighting conditions, such as infrared, ultraviolet, or the like.

For coating some very soft materials, retroreflective vinyl dispersions may be

applied by a hot-melt coating technique. On fusion, vinyl dispersions pass from the fluidity of a two phase dispersion, through a weak gel to a homogenous liquid hot melt. The viscosity of this melt depends on a number of factors, but notably the level of plasticizer. Therefore, with a high plasticizer content and the resulting very low dispersion viscosity, it is best to preheat and flux the dispersion, then flow the melt from a hopper-type coater onto the substrate. Because the dispersion must be held for a time at the melt temperature, excellent heat stabilization is of prime importance for this method of application.

Retroreflective vinyl dispersions are suited for casting onto substrates such as paper and non-woven materials. The adhesion of dispersion resin coatings to most paper substrates is good, however, for highly calendered papers, such as Kraft paper, it may be necessary to add modified rosin derivatives and other tackifiers to ensure adhesion. Papers treated with latex, or tapes utilizing rubber adhesives that are plasticizer sensitive, require additives such as polyester polymeric plasticizers to prevent migration into and softening of the continuous non-vinyl polymer. The dispersions may include materials such as coated and non-coated microspheres, metallic flake, metal oxides, nacreous pigment, titanium dioxide, or other refractive or reflective materials, to provide decorative and special visual effects if incorporated into one or more of the coatings, and may include ingredients that are only visible when viewed in particular lighting conditions, such as infrared, ultraviolet, or the like.

Spread coating is widely used to produce roll goods. The relative processing ease makes retroreflective vinyl dispersions highly suitable for calendered materials, thin films which can be made strain-free, and for chemically blown films. The reflective dispersions may be 100% solids with no solvent removal needed, therefore, thick coatings may be

applied in a single pass and the cost of solvents and of the heat for solvent vaporization is eliminated. Many spread coated products do not involve a permanently attached substrate, decals and decorative roll goods films may be manufactured by applying the retroreflective vinyl dispersions on a previously printed release paper, fusing and then applying a solvent based adhesive over the back of the dispersion. The release paper is designed so that the printing pattern transfers from the paper to the dispersion. When unrolled, the adhesive mass is temporarily attached to the bottom surface of the release paper, and the product is right side up. Because the dispersion can be applied to a substrate, fused and cooled thoroughly before stripping, the likelihood of inducing strains by distorting warm or hot film is reduced. The spread coating dispersions and the printed formulations on the release papers may include materials such as coated and non-coated microspheres, metallic flake, metal oxides, nacreous pigment, titanium dioxide, or other refractive or reflective materials, to provide decorative and special visual effects when incorporated into one or more of the coatings, and may include ingredients that are only visible when viewed in particular lighting conditions, such as infrared, ultraviolet, or the like.

Other than the carboxyl-functional polymers, retroreflective vinyl dispersions do not readily adhere to metal substrates, particularly those used in coil coating. Coil coating is a process in which metal is coated on a flat form, coiled and subsequently uncoiled and formed into finished articles. Therefore it is necessary to pre-treat the substrate with a solvent based adhesive primer, such as nitrile/phenolic/epoxy combinations, followed by flash baking or partial curing before application of retroreflective dispersions.

The technique of dip saturation may be used to obtain thorough saturation of a

product with retroreflective dispersions. Squeeze-rollers drive out the air and yield a homogenous vinyl mass between the fibres, the excess compound is doctored off both surfaces of the material before it enters the fusion oven.

In curtain coating, the retroreflective dispersions flow from a slit in a hopper shaped container onto articles or materials passing through on a conveyer beneath. The dispersion bypassing the articles or materials enters a catch basin beneath the conveyer.

Dip moulding may also be used to apply the retroreflective vinyl dispersions to various products. This process consists of dipping a mould into the dispersion, then fusing the coating that remains on the mould. There are many versions of the process, such as hot or cold dipping, or both, or more than one dip for special visual effects. The retroreflective coating may be stripped from the mould or the coating may become part of the finished product.

Rotational moulding involves loading the moulds with the retroreflective dispersions, rotating and fusing the part, cooling the part and unloading. In the casting and fusing stage, the mould is rotated in two planes, perpendicular to one another. As heat penetrates the mould, the dispersion is gelled and builds up in an even distribution on the interior wall surface of the moulds, the mould is then cooled and the product removed. The retroreflective dispersions should have a low viscosity at a low shear and little or no yield value, the viscosity should be in the range of 1000 to 8000 centipoise, this range provides the dispersion with the greatest opportunity to wet and mould prior to gelation.

Slush moulding is a method of producing hollow objects. The basic process involves filling a hollow mould with a retroreflective dispersion, exposing the mould to heat, gelling an inner layer in the mould, inverting the mould and pouring out the excess

of the dispersion, and then heating the mould to fuse the dispersion, the mould is then cooled and the product removed. The process may be a single pour method or multiple pour after partially gelling the first layer.

Retroreflective vinyl dispersions may be used as coatings on filaments, wires and woven cords, and similar materials. There are generally three methods of strand coating, the set-die method, the floating-die method, and a method that does not use a die. In formulating for strand coating, both the requirements of the end use and the processing conditions must be considered. In coating wire, thread or woven cords, it must be determined whether the dispersion should penetrate the strand or coat the surface. The fusion of the strand coatings is dependent upon the speed of travel, length of oven or tower, the fusion temperatures available and the thickness of the coating.

The retroreflective vinyl dispersions may also be applied by spraying, because of their easier flow, but extra body, vinyl dispersions may be applied as heavy coatings on vertical surfaces without sags. The flow properties of vinyl dispersions for spraying are important, both low and high shear conditions are encountered. Standard spray guns may be used, by using special spray heads, decorative veil and spatter patterns may be applied. The spray gun orifices must be of a size to allow the largest particles or microspheres to pass through easily. In passing through the orifices at pressures ranging from about 30 to 100 psi, the dispersions undergo a high degree of shear, then upon being deposited on the substrate, the low-shear flow properties of the dispersion will dictate how smooth a film will result, and how much can be laid without sags or runs.

EXAMPLE 1.

The following formulation was mixed in the order listed while continuous stirring took place, at a medium speed with a conventional dispersion mixer, for 30 minutes. The dispersion was then applied to a 50/50 cotton/polyester blend fabric using a manual screen printer through a 110 (43 cm) polyester mesh. A single fill pass was made, followed by a single print pass. The printed fabric was then passed through a heated chamber set at 160°C (350°F) for 90 seconds.

<u>Component</u>	<u>Parts Per 100 Resin</u>
Polyvinyl chloride resin	100
Polymeric plasticizer	60
Barium/Cadium (Zinc) stabilizer	2.5
Mineral spirits	5
Metallized Microspheres	50
Silane	0.4
Poly-isocyanurate bonding agent	5
Colour pigment	3

EXAMPLE 2.

The following formulation was mixed in the order listed while continuous stirring took place, at a medium speed with a conventional dispersion mixer for 30 minutes. The dispersion was then applied to an undyed 100% cotton fabric using a manually operated draw-down rod with 50 micron openings, in a single pass. The fabric was then passed

through a heated chamber set at 165°C (330°F) for 120 seconds.

<u>Component</u>	<u>Parts Per 100 Resin</u>
Polyvinyl chloride resin	100
Polymeric plasticizer	50
Di-2-ethylhexyl phthalate	10
Phthalic anhydride	10
Methyl isobutyl ketone	5
Barium/Cadium (Zinc) stabilizer	2.5
Metallized Microspheres	50
Silane	0.5
Colour pigment	5

CLAIMS

What is claimed is:

1. A retroreflective coating composition comprising of a dispersion of polyvinyl chloride resins, plasticizers, stabilizers, fillers and additives, colour pigments, adhesion promoting agents, and refractive and retroreflective constituents. Which when applied to a substrate and subjected to heat, is converted from a liquid dispersion to a thermoplastic solid offering retroreflective properties.
2. A composition according to claim 1 wherein the dispersion includes transparent spheres with a refractive index of between 1.3 and 2.5 and a size ranging from 5 to 250 microns in diameter.
3. A composition according to the preceding claims wherein the dispersion includes transparent spheres partially or totally covered with aluminium, silver, alloys, oxides or other metallic or chemical coatings to provide a reflecting surface, and applied to the spheres by vapour or chemical deposition procedures.
4. A composition according to the preceding claims wherein the dispersion includes transparent spheres partially or totally covered with alternating layers of high and low refractive index materials, such as, but not exclusively, layers of zinc sulfide and magnesium fluoride, applied by vapour or chemical deposition procedures.
5. A composition according to the preceding claims wherein the dispersion includes transparent spheres partially or totally covered with a transparent coating containing reflective or refractive particles, such as, but not exclusively, metallic flake, metal oxides, nacreous pigments, and titanium dioxide.
6. A composition according to preceding claims wherein the dispersion includes transparent coloured spheres.
7. A composition according to preceding claims wherein the dispersion includes

spheres which are coated partially or totally with one or more coloured layers.

8. A composition according to preceding claims wherein the content of spheres in a dispersion is between 5 to 300 parts per 100 vinyl resin (phr).
9. A composition according to preceding claims wherein the dispersion includes transparent spheres, and one or more of the following, metallic flake, metal oxides, nacreous pigments, titanium dioxide or other refractive or reflective materials.
10. A composition according to preceding claims wherein the dispersion includes transparent partially or totally coated spheres, and one or more of the following, metallic flake, metal oxides, nacreous pigment, titanium dioxide or other refractive or reflective materials.
11. A composition according to preceding claims wherein the dispersion includes transparent partially or totally coated spheres which are additionally coated with silanes and organosilanes or blends of silanes and organosilanes.
12. A composition according to claim 1 wherein the dispersion includes colour pigments. The term pigments also refers to dyes and other particles that result in the appearance of colours. The pigments may be organic or inorganic in nature and should be milled to a very fine particle size, the pigments should be materials that are soluble in polyvinyl chloride polymer and enter into the polymer matrix during the fusion process.
13. A composition according to claims 1 and 12 wherein the dispersion includes pearlescent, fluorescent, phosphorescent, and metallic pigments either separately or as blends.
14. A composition according to claim 1 wherein the dispersion includes volatile dispersants or thinners which are removed during the heating process.
15. The composition according to claim 1 wherein the vinyl dispersion resins are

polyvinyl chloride homopolymers and copolymers and may be monomodal, bimodal, or multimodal in a size range of 0.2 - 60 microns.

16. The composition according to claim 1 wherein the vinyl dispersion resins are blends of polyvinyl chloride homopolymers and copolymers, and may be monomodal, bimodal, or multimodal in a size range of 0.2 - 60 microns.
17. The composition according to claim 1 wherein the vinyl dispersions include functionally active resins, such as those with properties attributable to carboxyl groups on the vinyl chain.
18. The composition according to claim 1 wherein the vinyl dispersions include vinyl copolymer resins, these resins may have carboxyl, hydroxyl or other functionalities, that when crosslinked with epoxy, melamine, or other adhesion promoters, provide increased adhesion to a substrate.
19. A composition according to claim 1 wherein the dispersion includes plasticizers such as esters of long chain alcohols with aromatics such as phthalic anhydride, and straight-chain dibasic acids such as sebacic, azelaic, or adipic, or with phosphoric acids; or they may be polyesters such as those based on propylene glycol and sebacic acid.
20. A composition according to claim 1 wherein the dispersion includes phthalate esters plasticizers, such as di-2-ethylhexyl phthalate or shorter-chain-alcohol phthalate esters such as dihexyl and dibutyl phthalates.
21. A composition according to claim 1 wherein the dispersion includes longer-chain-alcohol phthalates.
22. A composition according to claim 1 wherein the dispersion includes phosphate ester plasticizers, such as tricresyl phosphate and octyldiphenyl phosphate.
23. A composition according to claim 1 wherein the dispersion includes highly solvating

plasticizers, such as butyl benzyl phthalate, dihexyl phthalate, diisohexyl phthalate, and esters of benzoic acid. These plasticizers are used with copolymer dispersion and extending resins to achieve usable physical properties at fusion temperatures below 138°C (280°F).

24. A composition according to claim 1 wherein the dispersion includes specialized monomeric esters such as trimellitates, including trioctyl trimellitate, trisooctyl trimellitate, trisononyl trimellitate, and similar esters of linear alcohols.
25. A composition according to claim 1 wherein the dispersion includes polymeric plasticizers, such as polyester of propylene glycol and sebacic acid.
26. A composition according to claim 1 wherein the dispersion includes epoxy, polymeric and citrate plasticizers.
27. A composition according to claim 1 wherein the dispersion includes low volatility acrylate monomers such as triethylene glycol dimethacrylate.
28. A composition according to claim 1 wherein the dispersion includes epoxidized soya and linseed oils providing heat and light stabilization properties as well as plasticization properties.
29. A composition according to claim 1 wherein the dispersion includes phosphates to provide a level of flame resistance through increased char formation during combustion.
30. A composition according to claim 1 wherein the dispersion includes primary stabilizers of leads, mixed metals, and organotin stabilizers, and secondary stabilizers of epoxidized oils and metallic soaps.
31. A composition according to claim 1 wherein the dispersion includes stabilizers based on barium, cadmium, and zinc salts of long-chain fatty acids such as stearic, oleic, benzoic, lauric acids, either individually or as blends.

32. A composition according to claim 1 wherein the dispersion includes antioxidants and ultraviolet stabilizers to minimize degradation during long term exposure to ultraviolet light and weathering.
33. A composition according to claim 1 wherein the dispersion includes aliphatic and aromatic diluents or blends of both.
34. A composition according to claim 1 wherein the dispersion includes dispersants such as diisobutyl ketone, methyl isobutyl ketone, methyl ethyl ketone, isophorone, cyclohexanone, diacetone alcohol and butyl carbitol, either individually or as blends.
35. A composition according to claim 1 wherein the dispersion includes viscosity modifiers that act by reducing the interparticle structure in the dispersion. Liquid surface active agents such as non-ionic or anionic type ethoxylated alcohols, fatty acid esters, aliphatic compounds, and lecithin-based derivatives act as viscosity depressants.
36. A composition according to claim 1 wherein the dispersion includes thickening agents. Organo-metallic complexes, fumed and precipitated silicas, bentonite clay, special clays, and ultrafine calcium carbonates offer a high degree of thixotropy.
37. A composition according to claim 1 wherein the dispersion includes liquid nitrile rubber to provide oil resistance and reduce plasticizer migration.
38. A composition according to claim 1 wherein the dispersion includes silanes and organosilanes either individually or as blends.
39. A composition according to claim 1 wherein the dispersion includes epoxy resins, modified phenolic and hydrocarbon resins, titanates, alkyl phosphate ester, zirconates and stabilized metal based adhesion promoters either individually or as blends.
40. A composition according to claim 1 wherein the dispersion includes iso-cyanurate

trimer in di-butyl phthalate to act as adhesion promoting agents.

41. A composition according to claim 1 wherein the dispersion is applied to a substrate by flat-bed screen printing.
42. A composition according to claim 1 wherein the dispersion is applied to a moving substrate by continuous flat-bed or rotary screen printing.
43. A composition according to claim 1, 41 and 42 wherein the dispersion is applied to a substrate over the whole surface area, or in selected designs and patterns, and may be single or multiple colours.
44. A composition according to claims 1 and 41 to 43 wherein the dispersions are applied to dark coloured substrates which are pre-printed with a light coloured underbase in sections, patterns, or as an all over print.
45. A composition according to claims 1 and 41 to 44 wherein the dispersions are applied to the substrate in multiple layers.
46. A composition according to claim 1 wherein the dispersions are screen printed onto a release or casting paper. The designs and images are printed in reverse order, starting with the eventual outer surface print. Each print is gelled before the application of the next. The printed release or casting material, is then applied to the substrate, with the print adjacent to the surface of the substrate, and is then subjected to heat and pressure to reactivate and fully fuse the vinyl dispersion to the substrate. The release paper is then peeled away to reveal the correctly facing printed image on the substrate.
47. A composition according to claims 1 and 45 wherein the dispersions are applied to a release paper or casting material that has been embossed or patterned to create textured effects on the outer surface.
48. A composition according to claims 1, 45 to 47 wherein the dispersions are applied

to release or casting materials in single or multiple layers, either as sections or as all over coverage.

49. A composition according to claims 1, 41 to 48 wherein the dispersions are applied in single or multiple layers of differing refractive indices, either as sections or as all over coverage.
50. A composition according to claim 1 wherein the dispersion includes small amounts of commercially available puff additives.
51. A composition according to claim 1 wherein the dispersion may be applied to moving lengths of substrate, such as fabrics, papers, metals, and plastics by knife-over-roll, floating-knife, and knife-over-blanket, systems.
52. A composition according to claims 1 and 49 wherein the dispersions are applied as one or more coatings.
53. A composition according to claim 1, 52 and 53 wherein the dispersions and one or all of the coatings include colour pigments.
54. A composition according to claims 1, 49 to 52 wherein the dispersions include ingredients to create decorative and special visual effects when incorporated into one or more of the coating layers, and include ingredients that are only visible when viewed in specific lighting conditions, such as infrared, ultraviolet, or the like.
55. A composition according to claim 1 wherein the dispersion is applied to moving lengths of substrate by roll coating. The retroreflective dispersion is picked up or supplied to a roller that travels in the same direction or opposite direction as the substrate. The dispersions may be fused by various devices, including ovens, heat platens, heat rolls, radiant resistance rods or quartz lamp heating.
56. A composition according to claims 1 and 55 wherein the dispersion is applied in one or more layers.

57. A composition according to claim 1 wherein the dispersion is applied in one or more finishing operations to a moving web, embossing is then carried out in-line, with an engraved steel roll applying pressure to the web as it passes over a rubber backup roll immediately at the oven exit. The fused reflective dispersion is chilled to set the emboss and allow it to release cleanly from the embossing roll.
58. A composition according to claims 1 and 57 wherein an unembossed dispersion is reheated by passing it over heated platens and embossed in a separate operation.
59. A composition according to claims 1 and 55 to 58 wherein a contrasting colour is applied in the emboss depression by means of a tight knife pass and top coating. Top coating protects exposed surfaces from abrasion, dirt, and stain pickup and need to be formulated with high molecular weight homopolymers to minimize plasticizer migration from the substrate.
60. A composition according to claims 1 and 57 to 59 wherein acrylic solution polymers and cellulose acetate butyrate blended with vinyl add to the blocking resistance and dryness of the coating.
61. A composition according to claim 1 wherein dispersions used in printing and flocking finishing operations, copolymer or carboxy functional dispersions are used as the adhesive.
62. A composition according to claim 1 wherein dispersions are applied by a hot-melt coating process. On fusion, vinyl dispersions pass from the fluidity of a two phase dispersion, through a weak gel to a homogenous liquid hot melt. The viscosity of this melt depends on a number of factors, principally the level of plasticizer. Therefore, with a high plasticizer content and the resulting low dispersion viscosity, the dispersion is preheated, the melt then flows from a hopper-type coater onto the substrate.

63. A composition according to claim 1 wherein the dispersions are applied by casting onto substrates such as paper and non-woven materials. For highly calendered substrates, modified rosin derivatives and other tackifiers should be added to ensure adhesion.
64. A composition according to claims 1 and 63 wherein the dispersions are applied by casting onto substrates treated with latex, or tapes utilizing rubber adhesives that are plasticizer sensitive, additives such as polyester polymeric plasticizers should be included to prevent migration into and softening of the continuous non-vinyl polymer.
65. A composition according to claim 1 wherein the dispersions are applied by spread coating onto roll goods.
66. A composition according to claims 1 and 65 wherein the dispersions are applied by spread coating onto a previously printed release paper, fusing and then applying a solvent based adhesive over the back of the dispersion. The release paper is designed so that the printed pattern transfers from the paper to the dispersion. When unrolled, the adhesive mass is temporarily attached to the bottom surface of the release paper, and the product is right side up. The dispersion can be applied to a substrate, fused and cooled thoroughly before stripping.
67. A composition according to claim 1 wherein the dispersions are applied by coil coating on to flat metal, coiled and subsequently uncoiled and formed into finished articles. The substrate should be pre-treated with a solvent based adhesive primer, such as nitrile/phenolic/epoxy combinations, followed by flash baking or partial curing before application of retroreflective dispersions.
68. A composition according to claim 1 wherein the dispersions are applied by the technique of dip saturation. Squeeze-rollers drive out the air and yield a

homogenous vinyl mass between the fibres, the excess compound is doctored off both surfaces of the material before it enters the fusion oven.

69. A composition according to claim1 wherein the dispersions are applied by curtain coating. The retroreflective dispersions flow from a slit in a hopper shaped container onto articles or materials passing through on a conveyer beneath.
70. A composition according to claim1 wherein the dispersions are applied by dip moulding. This process consists of dipping a mould into the dispersion, then fusing the coating that remains on the mould. The liquid dispersions may be hot or cold, and may be stripped from the mould or the coating may become part of the finished product.
71. A composition according to claim1 wherein the dispersions are applied by rotational moulding. Involving loading moulds with the retroreflective dispersions, rotating and fusing the part, cooling the part and unloading. In the casting and fusing stage, the mould is rotated in two planes, perpendicular to one another. As heat penetrates the mould, the dispersion is gelled and builds up in an even distribution on the interior wall surface of the moulds, the mould is then cooled and the product removed.
72. A composition according to claim1 wherein the dispersions are applied by slush moulding. The process may be a single pour method or multiple pour after partially gelling the first layer.
73. A composition according to claim1 wherein the dispersions are applied to filaments, wires, woven cords and the like, by strand coating using the set-die method, the floating-die method, and methods that do not require a die.
74. A composition according to claim 1 wherein the dispersions are applied by spraying.
75. A composition according to claim 1 wherein the dispersions are applied to non-polar

substrates such as polypropylene and polyethylene, the surfaces are pre-treated by passing the substrate between two electrodes and rendered polar to increase adhesion.

76. A composition according to claim 1 wherein the dispersions are applied to substrates pre-treated with solvents such as toluene and chlorinated hydrocarbons, or the like, to increase adhesion.
77. A composition according to claim 1 wherein the dispersions are applied to substrates pre-treated with chemical oxidising agents such as chromic acid, or the like, to increase adhesion.
78. A composition according to claim 1 wherein the dispersions are applied to substrates pre-treated by exposing the substrate to an oxidising flame for a short period to increase adhesion.



Application No: GB 9813786.2
Claims searched: 1-78

Examiner: Jason Scott
Date of search: 12 November 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.Q): C3V (VABN, VABQ, VABR, VACH, VACN, VACQ, VACR, VDQ, VEB)
Int CI (Ed.6): C08K (3/40); C09D (5/33, 127/06)
Other: ONLINE, WPI, EPODOC, JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0486319 A1 MATSUMOTO See page 3, lines 21-31.	1 at least.
X	EP 0305074 A2 3M See page 3, lines 36-40 and page 4, line 18.	1 at least.
X, E	WO 9904098 A1 3M See page 5, line 15-30.	1 at least
X	BE 892056 A GRIFFINE-MARECHAL See example 2.	1 at least
X	WPI Abstract Accession No. 1989-361148 & JP 1271436 A KOHKOKU (30.10.89) See abstract	1 at least.

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.